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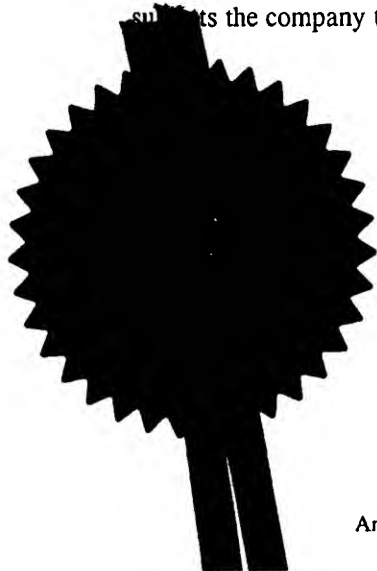
I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears a correction, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

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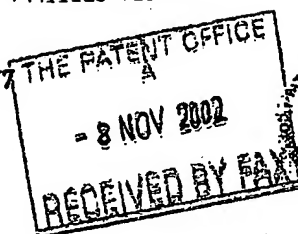
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Signed

Dated 27 February 2004

Patents Form 1/77

Patents Act 1977
(Rule 16)08NOV02 E76350-1 10063
P01/7700 0.0-0226010.7**Request for grant of a patent**

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form.)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

CDT 382

2. Patent application number

(The Patent Office will fill in this part)

0226010.7

F 8 NOV 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

~~Cambridge Display Technology Limited~~~~Greenwich House~~~~Madingley Rise~~~~Madingley Road~~~~Cambridge CB3 0TX~~

COVION ORGANIC

SEMICONDUCTORS GmbH

65926 FRANKFURT

GERMANY

Patents ADP number (if you know it)

08401457661

If the applicant is a corporate body, give the country/state of its incorporation

~~United Kingdom~~

AE 477 5.12.02

4. Title of the invention

POLYMERS FOR USE IN ORGANIC
ELECTROLUMINESCENT DEVICES

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom
to which all correspondence should be sent
(including the postcode)

IP Department
Cambridge Display Technology Limited
Greenwich House
Madingley Rise
Madingley Road
Cambridge
CB3 0TX

PC 001 12, Madingley Road
Blackley, Manchester
M9 8L3

Patents ADP number (if you know it)

616644007

E1 7742125001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if

YES

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.

See note (d)

Patents Form 1/77

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Patents Form 1/77

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Continuation sheets of this form

Description 28

Claim(s) 3

Abstract -

Drawing(s) -

10. If you are also filing any of the following, state how many against each item.

Priority documents .

Translations of priority documents .

Statement of inventorship and right to grant of a patent (Patents Form 7/77) .

Request for preliminary examination and search (Patents Form 9/77) .

Request for substantive examination (Patents Form 10/77) .

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature

Date

08th November 2002

12. Name and daytime telephone number of person to contact in the United Kingdom Matthew Shade Tel: 01223 723514

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Polymers for use in organic electroluminescent devices

Background of the invention

Field of the invention

The present invention relates to organic semiconductive polymers comprising aryl substituted trans-indenofluorene repeat units, monomers for the preparation of such polymers, methods for the preparation of such polymers and the use of such polymers in organic optoelectronic devices.

Brief description of the prior art

Semiconductive organic polymers have been known for several decades. During the past ten years they have seen increasing application in the field of electroluminescent devices, also known as polymeric light emitting devices, see for example WO90/13148.

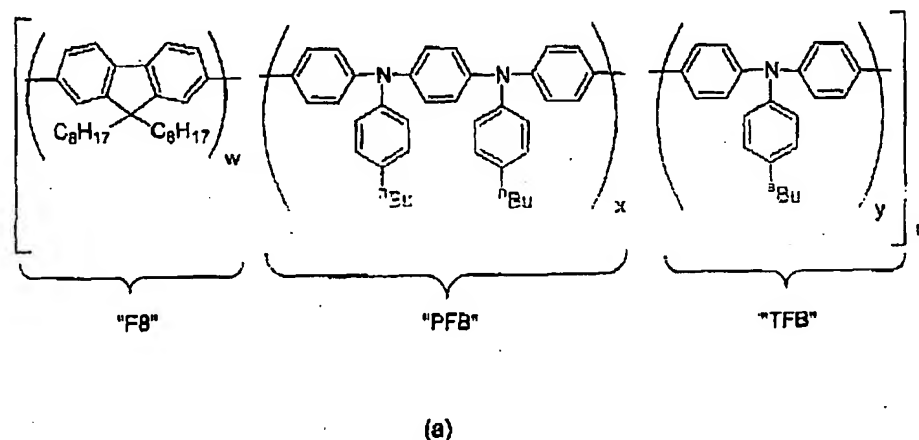
A polymeric light emitting device comprises a negative charge carrier injecting electrode, a positive charge carrier injecting electrode and a layer of polymeric light emitting material situated between the two electrodes. Application of a voltage between the two electrodes causes positive charge carriers, known as holes, to be injected from the positive charge injecting electrode and negative charge carriers, electrons, to be injected from the negative charge carrier injecting electrode. The holes and electrons combine in the layer of polymeric light emitting material to form an exciton which decays emitting light. The electroluminescent device may also comprise further layers for the transport of charge carriers from the electrodes to the layer of light emitting polymers, alternatively the light emitting polymer itself may incorporate charge transporting units in addition to light emissive units.

The nature of the polymeric material used in electroluminescent devices is critical to the performance of the device, materials used include poly(phenylenevinylenes), as disclosed in WO90/13148, polyfluorenes, as disclosed in WO97/05184, poly(arylamines), as disclosed in WO98/08773. Copolymers and blends of polymers have been found to be useful in such devices, as disclosed in WO92/03490,

WO99/54385, WO00/55927 and WO99/48160. Poly(arylamines) have been disclosed in which the aromatic groups may comprise heteroaromatic moieties such as triazine, see WO01/49789. In copolymers and blends of polymers different monomer units are used to provide different functions in the device, namely electron transport, hole transport and light emission.

In particular chains of fluorene repeat units, such as homopolymers or block copolymers comprising dialkylfluorene repeat units, may be used as electron transporting materials. In addition to their electron transporting properties, polyfluorenes have the advantages of being soluble in conventional organic solvents and have good film forming properties. Furthermore, fluorene monomers are amenable to Yamamoto polymerisation or Suzuki polymerisation which enables a high degree of control over the regioregularity of the resultant polymer.

One example of a polyfluorene based polymer is a blue electroluminescent polymer of formula (a) disclosed in WO 00/55927:



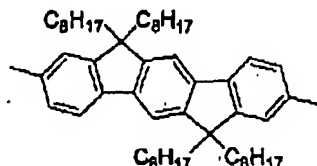
wherein $w + x + y = 1$, $w \geq 0.5$, $0 \leq x + y \leq 0.5$ and $n \geq 2$.

In this polymer, chains of dioctylfluorene, denoted as F8, function as the electron transport material; the triphenylamine denoted as TFB functions as the hole transport material and the bis(diphenylamino)benzene derivative denoted as PFB functions as the emissive material.

There are a number of disadvantages associated with fluorene based polymers which have led to a search for alternative electron transporting and light emitting units. These disadvantages include the limited hole transporting ability of the fluorene

units, the tendency of fluorene units to aggregate and the fact that when blue light emission occurs from fluorene based polymers the emission does not occur in the region of the electromagnetic spectrum in which the human eye is most sensitive.

In an effort to provide alternatives to fluorene based polymers, light emitting polymers comprising the tetraoctyl substituted trans-indenofluorene units shown below have been described in Marsitzky *et al*, Advanced Materials, 2001, 13, 1096-1099.

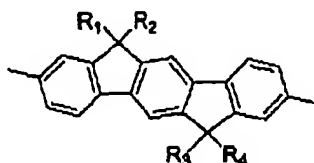


Polymers comprising such tetraoctyl trans-indenofluorene units are described as having a bathochromically shifted emission wavelength which leads to a blue emission colour matched to the sensitivity of the human eye.

The present inventors have further determined that trans-indenofluorenes are more stable to hole transport than fluorenes. In order to provide a range of trans-indenofluorenes with wider application in light emitting devices the present inventors show that by providing at least one aryl or heteroaryl substituent on the trans-indenofluorene unit it is possible to provide trans-indenofluorenes with a higher electron affinity and therefore improved electron injecting and transporting properties. A further advantage of the aryl substituted trans-indenofluorenes of the present invention is that polymers comprising these units have a higher Tg (glass transition temperature) and are therefore more stable and provide longer lived light emitting devices.

Summary of the invention

In a first embodiment the present invention provides polymers comprising optionally substituted first repeat units of formula (I):



(I)

wherein R_1 , R_2 , R_3 and R_4 are selected from hydrogen, alkyl, alkoxy, aryl, aryloxy or heteroaryl groups provided that at least one of R_1 , R_2 , R_3 and R_4 comprises an aryl or heteroaryl group.

In a preferred embodiment at least two of R_1 , R_2 , R_3 and R_4 comprise an aryl or heteroaryl group. Alternatively at least three of R_1 , R_2 , R_3 and R_4 comprise an aryl or heteroaryl group or each of R_1 , R_2 , R_3 and R_4 may comprise an aryl or heteroaryl group.

In a particularly preferred embodiment R_1 and R_2 comprise an aryl or heteroaryl group and R_3 and R_4 comprise an alkyl group.

Suitable aryl groups include phenyl, substituted phenyl, in particular alkyl substituted phenyl groups such as 4-octyl-phenyl and 4-*tert*-butyl-phenyl, fluoroalkyl substituted phenyls such as 4-(trifluoromethyl)phenyl, alkoxy substituted phenyl, such as 4-(2-ethylhexyloxy)phenyl and 4-methoxyphenyl, fluorinated phenyls, such as perfluorophenyls and 4-fluorophenyl and aryl substituted phenyls such as 4-(phenyl)phenyl. Suitable heteroaryl groups include pyridine, triazine, thiophene, pyrrole and furan, the heteroaryl groups may be substituted with alkyl, alkoxy, fluoro, fluoroalkyl, aryl or heteroaryl substituents.

Where one of R_1 , R_2 , R_3 and R_4 comprises an alkyl group suitable alkyl groups include octyl, *tert*-butyl, methyl, hexyl, perfluorooctyl or perfluorohexyl. Where one of R_1 , R_2 , R_3 and R_4 comprises an alkyl group the most preferred alkyl group is octyl.

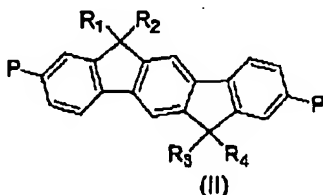
It is particularly advantageous if the aryl group comprises an optionally substituted phenyl group. 4-octylphenyl and 4-*tert*-butyl-phenyl substituents are preferred.

Where R_1 and R_2 comprise an aryl or heteroaryl group and R_3 and R_4 comprise an alkyl group it is preferred that R_1 and R_2 are selected group 4-octylphenyl and 4-*tert*-butyl-phenyl substituents and that R_3 and R_4 comprises octyl substituents.

The polymers of the present invention may be homopolymers or copolymers. Suitable copolymers may comprise two, three or more distinct monomer units. In a preferred embodiment the polymer of the present invention comprises a second

repeat unit, preferably this repeat unit comprises a triarylamine or a heteroaromatic. Preferred triarylamine comonomers include N,N-di(4-phenyl)-N-(4-sec-butylphenyl)amine ("TFB") and Di [N-(4-phenyl)-N-(4-n-butylphenyl)]-phenylene-1,4-diamine ("PFB").

The polymers of the present invention may be prepared by any suitable method. Suitable monomers for the preparation of the polymers of the present invention include a monomer comprising an optionally substituted compound of formula (II):



wherein each P independently represents a polymerisable group and R_1 , R_2 , R_3 and R_4 are as defined above. Preferably each P is independently selected from a reactive boron derivative group selected from a boronic acid group, a boronic ester group and a borane group and a reactive halide group.

The polymers of the present invention are suitably prepared by aryl-aryl coupling such as Yamamoto coupling or Suzuki coupling, Suzuki coupling is preferred.

The present invention is also directed to a process for preparing a polymer comprising a step of reacting a first monomer as defined above and a second monomer that may be the same or different from the first monomer under conditions so as to polymerise the monomers. This process preferably comprises polymerising in a reaction mixture:

- (a) a monomer as defined above wherein each P is a boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two reactive halide functional groups; or
- (b) a monomer as defined above wherein each P is a reactive halide functional group, and an aromatic monomer having at least two boron derivative functional groups selected from boronic acid groups, boronic ester groups and borane groups; or

(c) a monomer as defined above wherein one P is a reactive halide functional group and one P is a boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group,

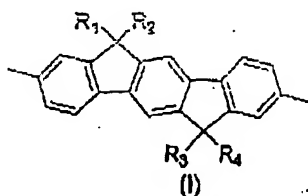
wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into boronate anionic groups.

The present invention is further directed organic light emitting devices comprising polymers of the present invention. In particular the polymers of the present invention may function as the electron transporting or light emissive components of an organic light emitting device.

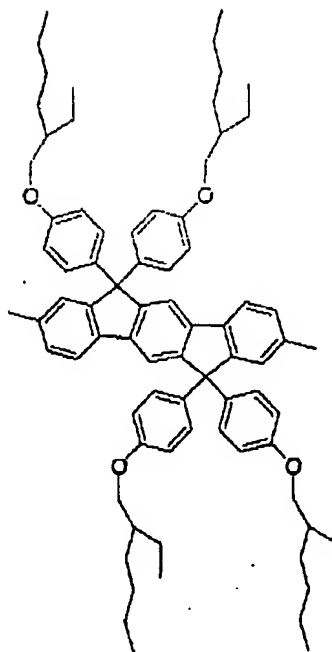
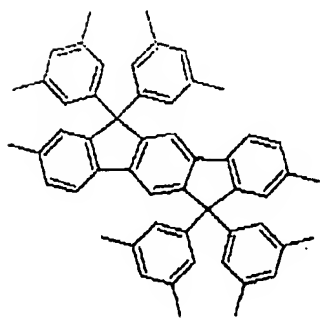
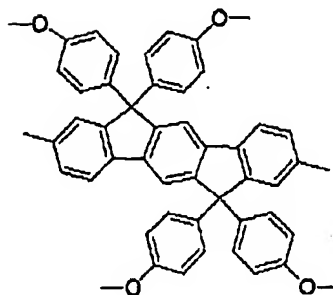
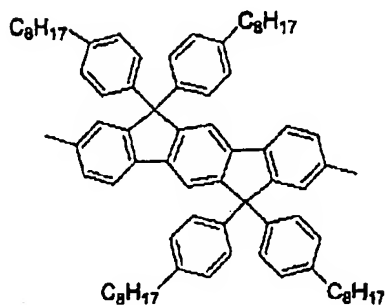
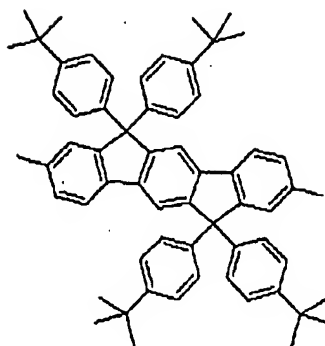
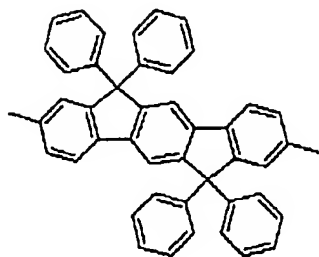
Detailed description of the invention

Description of preferred embodiments

The present invention is directed to polymers comprising repeat units of the formula (I):



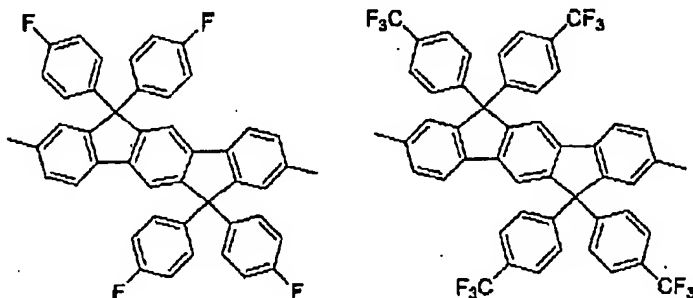
wherein at least one of substituents R₁, R₂, R₃ and R₄ comprises an aryl or heteroaryl group. The substituents R₁, R₂, R₃ and R₄ may all comprise the same aryl or heteroaryl group, examples of such repeat units include:



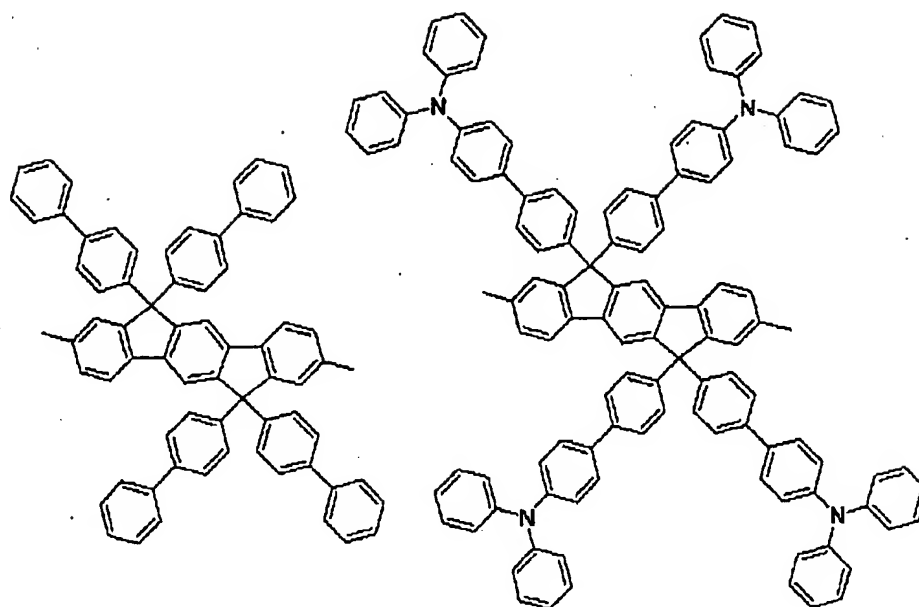
Substitution of the aryl groups with one or more alkyl chains comprising 4 to 12 carbon atoms has been found to improve the solubility of the polymers and also to limit aggregation of the polymer chains.

The aryl groups may also be substituted with fluoro or fluoroalkyl groups. In particular long chain perfluoroalkyl substituents are considered to reduce aggregation of the polymer chains. A further advantage of fluoro and fluoroalkyl substituted aryl groups is that the electron withdrawing properties of these groups increases the LUMO of the polymer and so enables more efficient electron injection into the polymer.

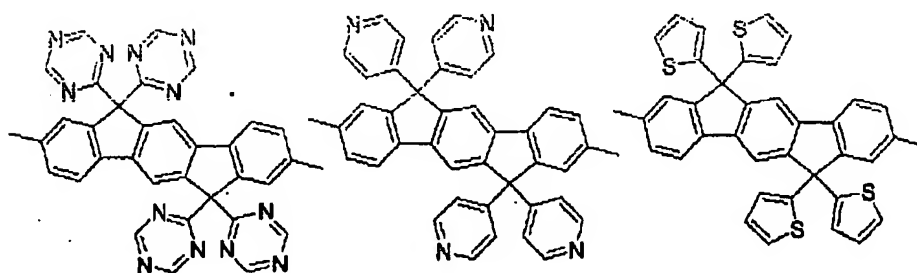
Examples of fluorine substituted repeat units include:



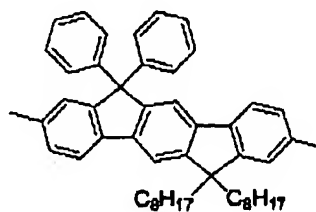
The aryl groups may be substituted with other aryl groups such as phenyl and substituted phenyl groups, as shown by the repeat units below:



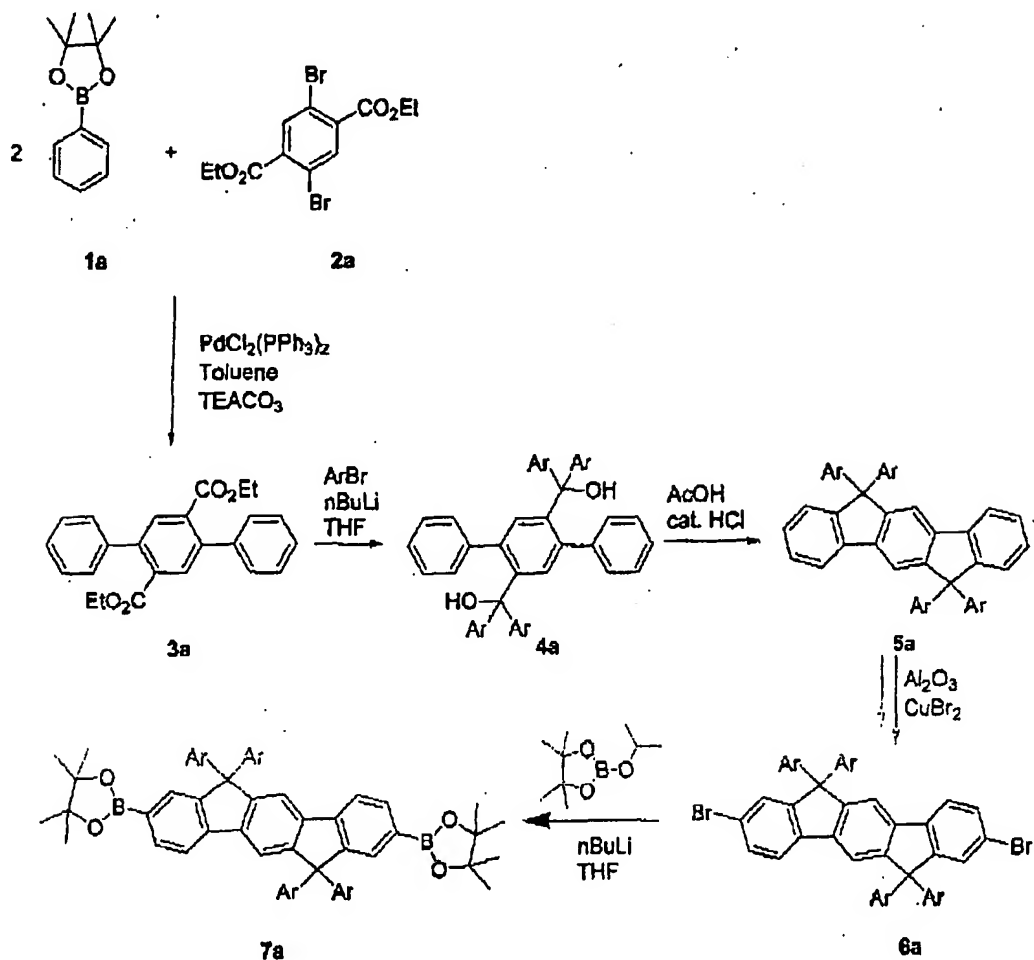
The repeat units may be substituted with heteroaryl groups, in particular substituents based on pyridine, triazine and thiophene are considered to be useful:



The polymers of the present invention may also comprise repeat units where the substituents R_1 , R_2 , R_3 and R_4 are not identical. For example R_1 and R_2 may comprise aryl substituents and R_3 and R_4 alkyl substituents, as shown below:



Indenofluorenes, alkyl triaryl trans-indenofluorenes and trialkyl aryl trans-indenofluorenes are now described.

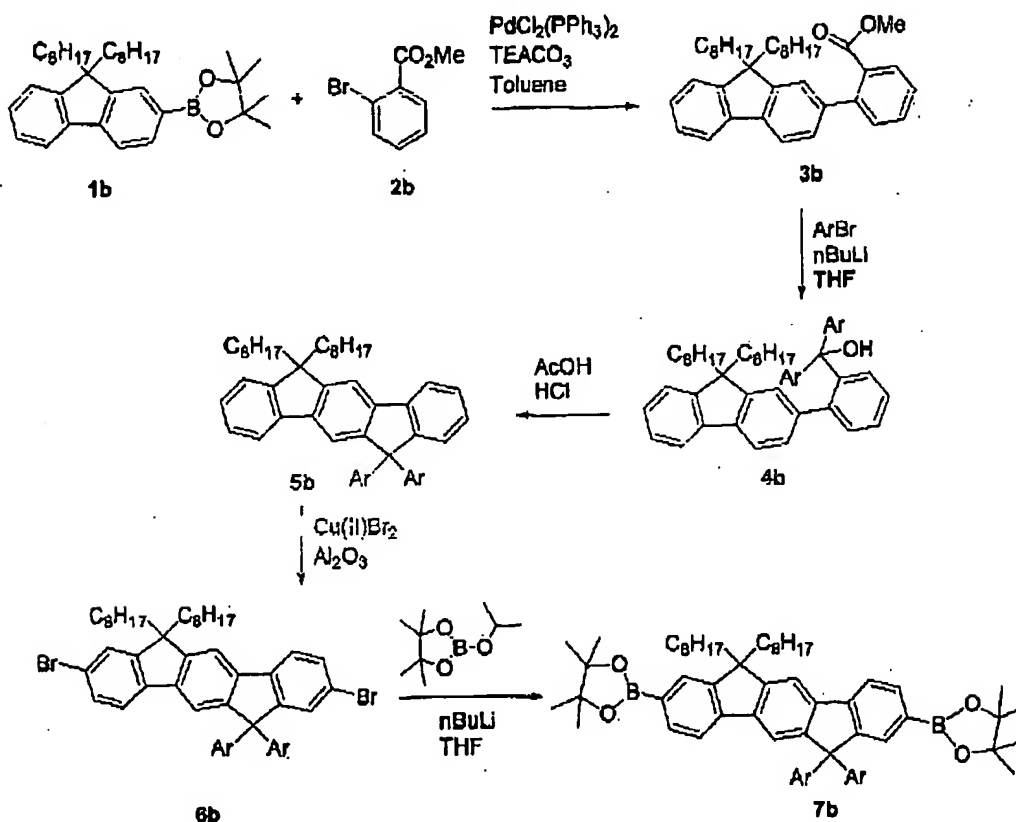


Scheme 1

Scheme 1 illustrates a method for the preparation of a tetra-aryl substituted monomer. Two equivalents of boronic ester **1a** are coupled to dibromo aromatic compound **2a** by Suzuki coupling using a palladium catalyst and a tetraethylammonium carbonate base. Compound **3a** forms the starting material from which a wide variety of tetra-aryl substituted trans-indenofluorenes may be prepared. Compound **3a** is reacted with four equivalents of a metallated aromatic compound

forming intermediate **4a** which is heated in glacial acetic acid in the presence of HCl to form the tetra-aryl substituted trans-indenofluorene **5a**. In order to prepare monomers suitable to undergo Suzuki or Yamamoto coupling the compound **5a** is brominated. The dibrominated compound **5a** may be further reacted with a boronic ester to form a boronic diester **7a**.

Scheme 2 below illustrates the preparation of a dialkyl diaryl substituted trans-indenofluorene.



Scheme 2

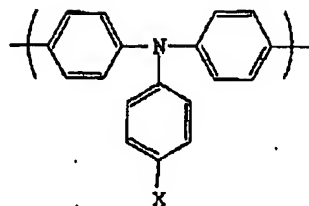
The boronic ester of a suitably substituted fluorene is prepared. In Scheme 2 the fluorene **1b** is a 9,9-dioctylfluorene. The boronic ester **1b** undergoes Suzuki coupling with a 2-bromobenzoate **2b** to form the terphenyl compound **3b**. The terphenyl compound **3b** is then reacted with two equivalents of a metallated aromatic compound to form intermediate **4b**. Intermediate **4b** is heated in glacial acetic acid to

form the dialkyl diaryl trans-indenofluorene 5b. The dialkyl diaryl trans-indenofluorene may be further reacted to form the polymerisable compounds 6b and 7b.

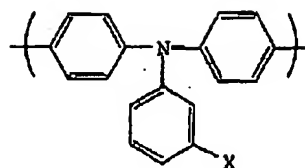
Scheme 2 illustrates a method for the formation of a dialkyl diaryl trans-indenofluorene, in order to prepare, for example, alkyl triaryl trans-indenofluorenes or trialkyl aryl trans-indenofluorenes it is necessary that the starting compound 1b comprises a 9,9-unsymmetrically substituted fluorene. Suitable 9,9-unsymmetrically substituted fluorenes are disclosed in WO 00/22028 and DE 19846767.

The polymers of the present invention may be homopolymers or copolymers. The use of monomers with different electronic properties in copolymers allows a greater degree of control over the electronic and light emissive properties of the polymer. A wide range of comonomers for polymerisation with the monomers of the invention will be apparent to the skilled person. Examples of comonomers include triaryl amines as disclosed in, for example, WO 99/54385 and heteroaryl units as disclosed in, for example, WO 00/46321 and WO 00/55927.

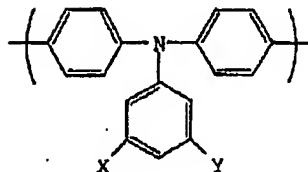
Particularly preferred triarylamine repeat units for such copolymers include units of formulae 1-6:



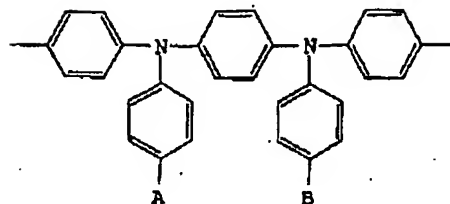
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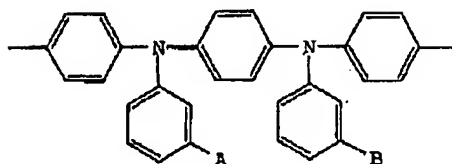
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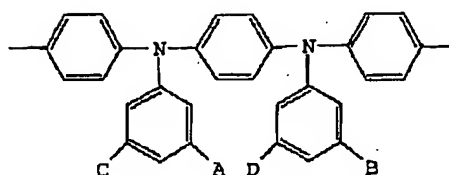
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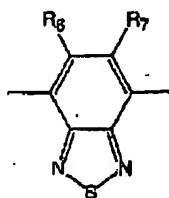
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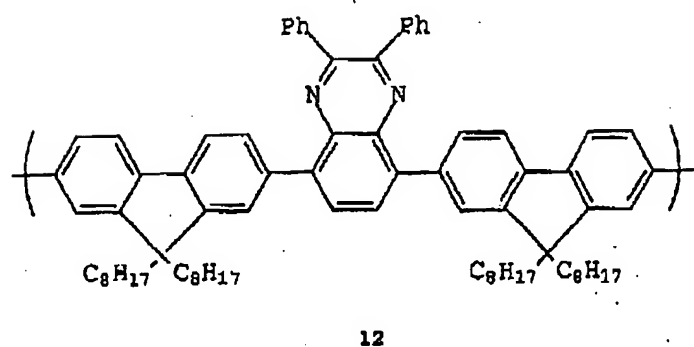
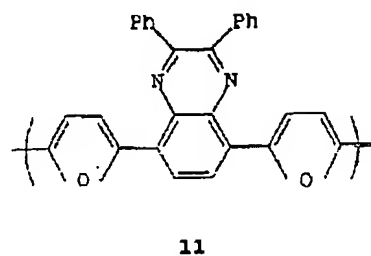
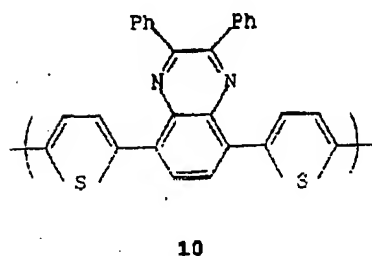
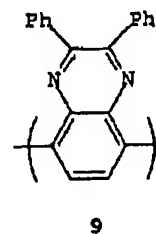
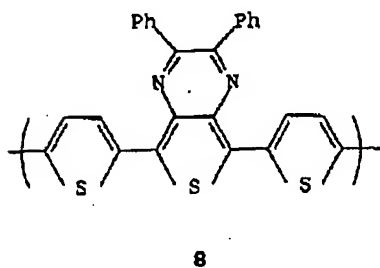
X and Y may be the same or different and are substituent groups. A, B, C and D may be the same or different and are substituent groups. It is preferred that one or more of X, Y, A, B, C and D is independently selected from the group consisting of alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl and arylalkyl groups. One or more of X, Y, A, B, C and D also may be hydrogen. It is preferred that one or more of X, Y, A, B, C and D is independently an unsubstituted, isobutyl group, an n-alkyl, an n-alkoxy or a trifluoromethyl group because they are suitable for helping to select the HOMO level and/or for improving solubility of the polymer.

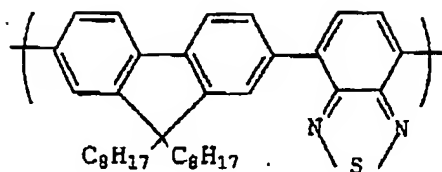
Particularly preferred heteroaryl repeat units for such copolymers include units of formulae 7-21:



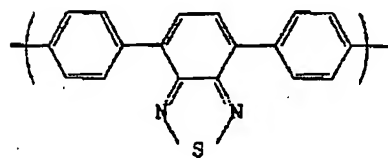
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wherein R_6 and R_7 are the same or different and are each independently a substituent group. Preferably, one or both of R_6 and R_7 may be selected from hydrogen, alkyl, aryl, perfluoroalkyl, thioalkyl, cyano, alkoxy, heteroaryl, alkylaryl, or arylalkyl. These groups are preferred for the same reasons as discussed in relation to X, Y, A, B, C and D above. Preferably, for ease of manufacture, R_6 and R_7 are the same. More preferably, they are the same and are each a phenyl group.

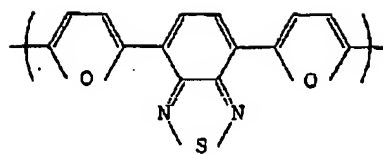




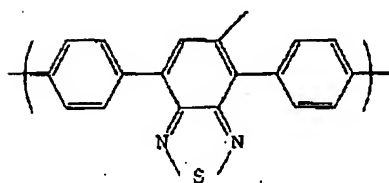
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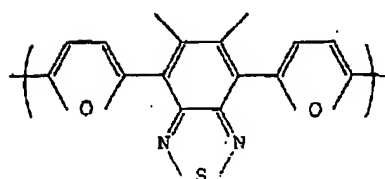
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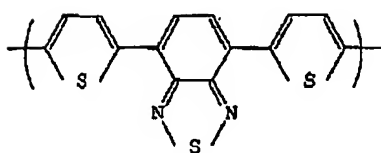
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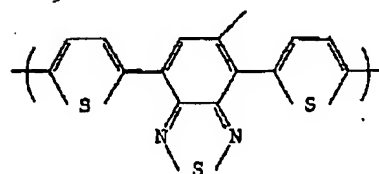
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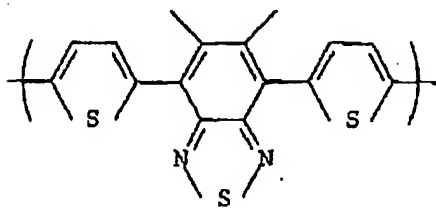
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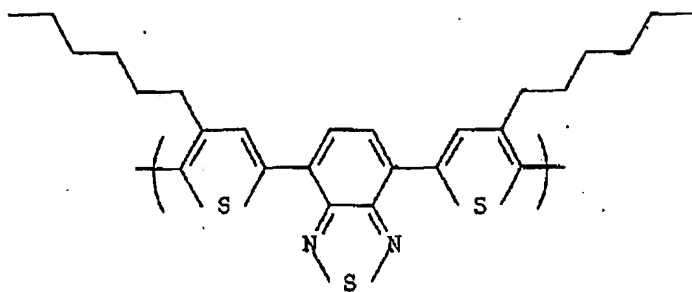
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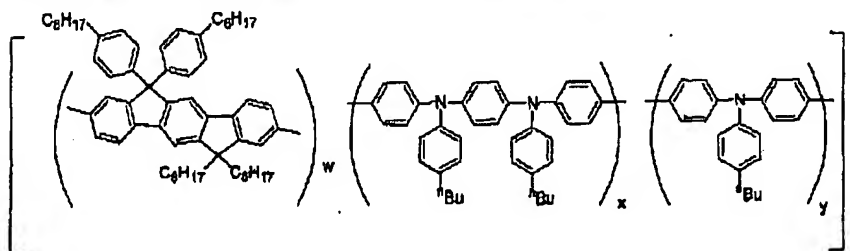


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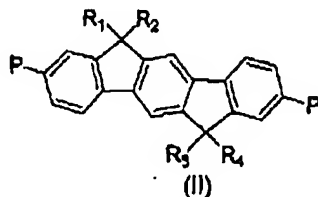


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The trans-indenofluorene repeat units of the present invention can act as efficient electron transporting units and light emitting units. It is therefore beneficial to combine the aryl substituted trans-indenofluorenes with hole transporting moieties such as triaryl amines to provide polymers having electron and hole transporting and light emitting properties. A particularly useful example of such a polymer is the copolymer of a dialkyl diaryl trans-indenofluorene, TFB and PFB shown below, wherein $w + x + y = 1$, $w \geq 0.5$, $0 \leq x + y \leq 0.5$ and $n \geq 2$.



The polymers of the present invention are prepared by the polymerisation of monomers of formula (II):



where P is a polymerisable group. Preferably P is a boron derivative group such as a boronic ester or a reactive halide such as bromine.

Preferred methods for polymerisation of these monomers are Suzuki polymerisation as described in, for example, WO 00/53656 and Yamamoto polymerisation as described in, for example, T. Yamamoto, "Electrically Conducting And Thermally Stable *pi*-Conjugated Poly (arylene)s Prepared by Organometallic Processes", Progress in Polymer Science 1993, 17, 1153-1205 or Stille coupling. For example, in the synthesis of a linear polymer by Yamamoto polymerisation, a monomer having two reactive halide groups P is used. Similarly, according to the method of Suzuki polymerisation, at least one reactive group P is a boron derivative group. Suzuki polymerisation may be used to prepare regioregular, block and random copolymers. In particular, random copolymers may be prepared when one reactive group P is a halogen and the other reactive group P is a boron derivative group. Alternatively, block or regioregular, in particular AB, copolymers may be prepared when both reactive groups of a first monomer are boron and both reactive groups of a second monomer are halide.

The aryl substituted trans-indenofluorenes of the present invention have particular application in organic light emitting devices. Organic light emitting devices comprise a layered structure comprising a lower electrode situated on a substrate, a layer, or several layers, of organic light emitting material and an upper electrode. When a voltage is supplied across the electrode of the device opposite charge carriers, namely electrons and holes, are injected into the organic light emitting material. The electrons and holes recombine in the layer of organic light emitting material resulting in the emission of light. One of the electrodes, the anode, comprises a high work function material suitable for injecting holes into the layer of organic light emitting material, this material typically has a work function of greater than 4.3 eV and may be selected from the group comprising indium-tin oxide (ITO), tin oxide, aluminum or

indium doped zinc oxide, magnesium-indium oxide, cadmium tin-oxide, gold, silver, nickel, palladium and platinum. The anode material is deposited by sputtering or vapour deposition as appropriate.

The other electrode, the cathode, comprises a low work function material suitable for injecting electrons into the layer of organic light emitting material. The low work function material typically has a work function of less than 3.5 eV and may be selected from the group including Li, Na, K, Rb, Be, Mg, Ca, Sr, Ba, Yb, Sm and Al. The cathode may comprise an alloy of such metals or an alloy of such metals in combination with other metals, for example the alloys MgAg and LiAl. The cathode preferably comprises multiple layers, for example Ca/Al, Ba/Al or LiAl/Al. The device may further comprise a layer of dielectric material between the cathode and the emitting layer, such as is disclosed in WO 97/42666. In particular it is preferred to use an alkali or alkaline earth metal fluoride as a dielectric layer between the cathode and the emitting material. A particularly preferred cathode comprises LiF/Ca/Al, with a layer of LiF of thickness from 1 to 10nm, a layer of Ca of thickness of 1 to 25nm and a layer of Al of thickness 10 to 500nm. Alternatively a cathode comprising BaF₂/Ca/Al may be used. The cathode materials are deposited by vacuum deposition.

For light emission to occur from the device it is preferred that either the cathode, the anode or both are transparent or semi-transparent. Suitable materials for transparent anodes include ITO and thin layers of metals such as platinum. Suitable materials for transparent cathodes include a thin layer of electron injecting material in proximity to the layer of organic light emitting material and a thicker layer of transparent conductive material overlying the layer of electron injecting material e.g. a cathode structure comprising Ca/Au. Where neither the cathode nor the anode is transparent or semi-transparent light emission occurs through the edge of the device.

The polymers of the present invention may comprise the light emissive layer of the device or may comprise an electron transport layer of the device. The polymers may be deposited by any suitable method although solution deposition methods are preferred. Solution deposition techniques include spin-coating, dip-coating, doctor blade coating, screen printing, flexographic printing and ink-jet printing. Ink-jet printing is particularly preferred as it allows high resolution displays to be prepared.

The organic light emitting device may include further organic layers between the anode and cathode to improve charge injection and device efficiency. In particular a layer of hole-transporting material may be situated over the anode. The hole-transport material serves to increase charge conduction through the device. The preferred hole-transport material used in the art is the conductive organic polymer polystyrene sulfonic acid doped polyethylene dioxythiophene (PEDOT:PSS) as disclosed in WO98/05187. Other hole transporting materials such as doped polyaniline or TPD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)[1,1'-biphenyl]-4,4'-diamine) may also be used. A layer of electron transporting or hole blocking material may be positioned between the layer of light emitting material and the cathode if required to improve device efficiency.

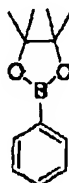
The substrate of the organic light emitting device should provide mechanical stability to the device and act as a barrier to seal the device from the environment. Where it is desired that light enter or leave the device through the substrate, the substrate should be transparent or semi-transparent. Glass is widely used as a substrate due to its excellent barrier properties and transparency. Other suitable substrates include ceramics, as disclosed in WO02/23579 and plastics such as acrylic resins, polycarbonate resins, polyester resins, polyethylene terephthalate resins and cyclic olefin resins. Plastic substrates may require a barrier coating to ensure that they remain impermeable. The substrate may comprise a composite material such as the glass and plastic composite disclosed in EP0949850.

The organic light emitting device is provided with an encapsulation means which acts to seal the device from the atmosphere. Suitable methods of encapsulation include covering the device on the cathode side with a metal can or glass sheet or providing an impermeable film over the device, such as a film comprising a stack of polymer layers and inorganic layers.

The invention is further described by means of the following examples.

Examples

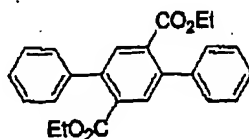
Synthesis of phenylboronic acid pinacol ester 1a



1a

Phenyl boronic acid (100 g, 0.82 mol, 1 equiv.) and pinacol (96.92 g, 0.82 mol, 1 equiv.) were dissolved in toluene (500 mL) at room temperature. The cloudy solution was then placed on to a rotary evaporator and stirred for 2 hours at 60 °C. After this period the solid had dissolved, concurrent with the formation of water (ca. 29.5 mL) as a second layer. The water was then removed in a separating funnel and the crude reaction filtered through Celite. Evaporation of the solvent yielded a clear pale yellow oil which solidified on cooling in a refrigerator to give the title compound in a near-quantitative yield as a white solid (ca. 157 g).

Synthesis of 1,4'-diphenyl-2,5-dicarboxylic acid diethylester 3a

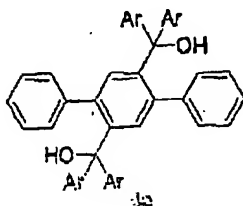


3a

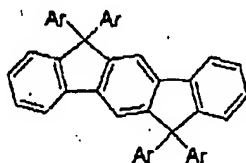
To a 3 L 3-neck flask equipped with a mechanical stirrer, reflux condenser and rubber septum was added phenyl boronic acid pinacol ester 2a (128.9 g, 0.63 mol, 2 equiv.) and 2,5-dibromo-1,4-dicarboxylic acid diethylester 1a (120 g, 0.32 mol, 1 equiv.) as a suspension in toluene (500 mL). A further 500 mL of toluene was then added and the reaction mixture briefly stirred before degassing using a nitrogen

purge for 1 hour at 40 °C. It was noted that there was a small amount of a pink insoluble residue from the dibromide. After this period dichloro bistrisphenyl phosphine palladium (II) (0.55 g, 0.78 mmol, 1/8 mol% per bromide) was added as a dry powder. The reaction mixture was then stirred under nitrogen for 15 minutes at 40 °C before the addition of tetra-*n*-ethylammonium carbonate (790 mL, ca. 33 wt% aqueous solution, 2 equiv. per arylboronate). The reaction was then stirred at 90 °C under nitrogen overnight (ca. 16 hrs.). TLC analysis at this point (DCM, silica plates) revealed a bright fluorescent blue spot (*R_f* ca. 0.6) and the absence of any starting material. Once the reaction mixture had cooled the aqueous layer was extracted and the solvent removed under reduced pressure to yield a light brown solid residue which was recrystallised from methanol to give the title compound as white crystalline solid. Slow evaporation of the mother liquor provided a second crop of product (92 g total, 77 %, >99 % pure by GC).

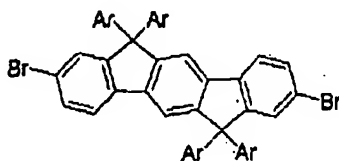
Syntheses of ter-phenyl tetra-aryldiol 4a



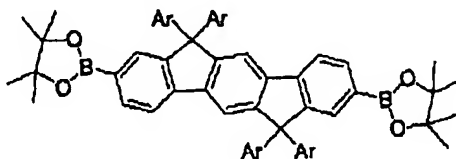
4-octylbromobenzene (4 equivs.) was dissolved in anhydrous THF at -78 °C. *n*BuLi (4 equivs., 2.5 M in hexanes) was then slowly added via a pressure equalised dropping funnel. After the addition the reaction was stirred for 30 minutes to insure complete transmetalation. 1,4'-diphenyl-2,5-dicarboxylic acid diethylester 3a (1 equiv.) was then slowly added as a solution in THF. The temperature was maintained at -78 °C throughout the operation. After a further 30 minutes the reaction was allowed to warm up to room temperature and stirring was continued over night (ca. 16 hours). After this period water was added to destroy any unreacted butyl lithium and the THF removed under reduced pressure. The crude reaction mixture was extracted into DCM and purified by titration from methanol.

Synthesis of 6,6', 12,12'-tetra-(4-octylbenzene)indeno[1,2-b]fluorene 5a**5a**

The arylated precursor 4a was heated in a mixture of glacial acetic acid and concentrated hydrochloric acid (a few drops) over night. After this period the reaction mixture was allowed to cool to room temperature before precipitation in to a large excess of rapidly stirred water. The crude product was collected by filtration and purified by crystallisation.

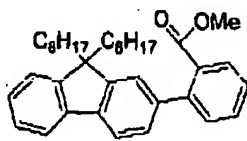
Syntheses of 2,8-dibromo-6,6', 12,12'-tetra-(4-octylbenzene)indeno[1,2-**6a****b]fluorene 6a**

Compound 5a was treated with copper (II) bromide supported on alumina, as described in Kodomari et al., *J. Chem. Soc.*, 1963, 1216.

Synthesis of 2,8-di(boronic acid pinacol ester)-6,6', 12,12'-tetra-(4-octylbenzene)indeno[1,2-b]fluorene 7a**7a**

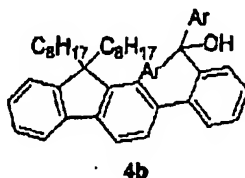
The title compound was prepared from compound 6a according to standard procedures see Ranger et al., *J. Chem. Soc., Chem. Commun.*, 1997, 1597.

Synthesis of 2-(2-methyl benzoate)-9,9-dioctylfluorene 3b

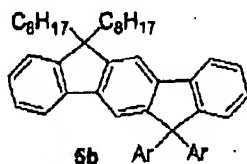


3b

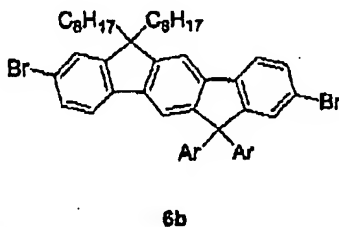
To a 3 L 3-neck flask equipped with a mechanical stirrer, reflux condenser and rubber septum was added 2-(boronic acid pinacol ester)-9,9-dioctylfluorene 1b (10 g, 21.72 mmol, 1 equiv.) and 2-bromomethyl benzoate 2b (4.67 g, 21.72 mmol, 1 equiv.) dissolved in toluene (100 mL) at room temperature. The solution was degassed using a nitrogen purge for 1 hour before dichloro bistrityl phosphine palladium (II) (20 mg, 0.027 mmol, 1/8 mol% per bromide) was added as a dry powder. The reaction mixture was then stirred under nitrogen for 15 minutes before the addition of tetra-*n*-ethylammonium carbonate (25 mL, ca. 33 wt% aqueous solution, 2 equiv. per arylboronate). The reaction was then stirred at 90 °C under nitrogen overnight (ca. 16 hrs.). TLC analysis at this point (DCM, silica plates) revealed a bright fluorescent blue spot (*R*_f ca. 0.6) and the absence of any starting material. Once the reaction mixture had cooled the aqueous layer was extracted and the solvent removed under reduced pressure to yield a yellow oil which was purified by recrystallisation to give the title compound.

Synthesis of 2-(phenyl-2,2-diarylmethyl)-9,9-dioctylfluorene 4b

Compound 4b was prepared in an analogous manner to compound 4a.

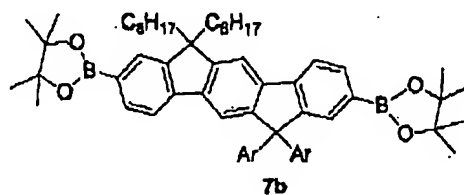
Synthesis of 6,6-dioctyl-12,12-di(4-octylbenzene)indeno[1,2b]fluorene 5b

Compound 5b was prepared in an analogous manner to compound 5a.

Synthesis of 2,8-dibromo-6,6-dioctyl-12,12-di(4-octylbenzene)indeno[1,2-b]fluorene 6b

Compound 6b was prepared in an analogous manner to compound 6a.

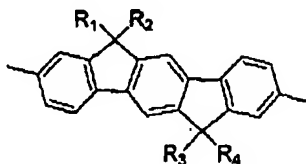
Synthesis of 2,8-di(phenylboronic acid pinacol ester)-6,6-dioctyl-12,12-di(4-octylbenzene)indeno[1,2-b]fluorene **7b**



Compound **7b** was prepared in an analogous manner to compound **7a**.

Claims

1. A polymer comprising optionally substituted first repeat units of formula (I):

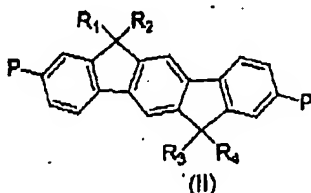


(I)

wherein R₁, R₂, R₃ and R₄ are selected from hydrogen, alkyl, alkoxy, aryl, aryloxy or heteroaryl groups provided that at least one of R₁, R₂, R₃ and R₄ comprises an aryl or heteroaryl group.

2. A polymer according to claim 1 wherein at least two of R₁, R₂, R₃ and R₄ comprise an aryl or heteroaryl group.
3. A polymer according to claim 1 wherein at least three of R₁, R₂, R₃ and R₄ comprise an aryl or heteroaryl group.
4. A polymer according to claim 1 wherein R₁, R₂, R₃ and R₄ comprise an aryl or heteroaryl group.
5. A polymer according to claim 1 wherein R₁ and R₂ comprise an aryl or heteroaryl group and R₃ and R₄ comprise an alkyl group.
6. A polymer according to any preceding claim wherein said aryl group comprises an optionally substituted phenyl group.
7. A polymer according to any preceding claim wherein said aryl group comprises a 4-octylphenyl group or a 4-*tert*-butyl-phenyl group.
8. A polymer according to any preceding claim comprising a second repeat unit.

9. A polymer according to claim 8 wherein said second repeat unit is selected from triaryl amines and heteroaromatics.
10. A monomer comprising an optionally substituted compound of formula (II):



- wherein each P independently represents a polymerisable group and R_1 , R_2 , R_3 and R_4 are as defined in any one of claims 1-7.
11. A monomer according to 10 wherein each P is independently selected from a reactive boron derivative group selected from a boronic acid group, a boronic ester group and a borane group and a reactive halide group.
12. A process for preparing a polymer comprising a step of reacting a first monomer as defined in any one of 10 or 11 and a second monomer that may be the same or different from the first monomer under conditions so as to polymerise the monomers.
13. A process for preparing a polymer according to claim 12 which comprises polymerising in a reaction mixture:
- (d) a monomer according to claim 10 wherein each P is a boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two reactive halide functional groups; or
 - (e) a monomer according to claim 10 wherein each P is a reactive halide functional group, and an aromatic monomer having at least two boron derivative functional groups selected from boronic acid groups, boronic ester groups and borane groups; or
 - (f) a monomer according to claim 10 wherein one P is a reactive halide functional group and one P is a boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group.

wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and a base in an amount sufficient to convert the boron derivative functional groups into boronate anionic groups.

14. An organic light emitting device comprising a polymer according to any of claims 1 to 9.